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Coordination Chemistry Reviews 144 (1995)
1–38

COORDINATION CHEMISTRY REVIEWS

# High-valent oxomanganese clusters: structural and mechanistic work relevant to the oxygen-evolving center in photosystem II

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Received 7 January 1994; in revised form 27 February 1995

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*SSDI* 0010-8545(95)01147-1

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**Abstract**

Recent years have seen a considerable interest in bioinorganic chemistry; in particular, the structural and functional modeling of active sites of metalloproteins. The oxomanganese tetramer in the $O_2$-evolving center (OEC) in photosystem II (PS II) of plants is thought to be the site of water oxidation to dioxygen. In conjunction with biophysical studies on the enzyme, inorganic chemists are trying to understand the structural and mechanistic aspects of the OEC by studying oxomanganese clusters. A number of such clusters, varying in nuclearity, ligation, and type and number of oxo-bridges, have been synthesized and characterized. Chemical, electrochemical and magnetic properties of these clusters have given much insight into the structure and function of the native enzyme. Here, we review recent efforts in inorganic model complex chemistry towards modeling the tetramanganese active site of PS II.

*Keywords:* Oxomanganese clusters; Photosystem II; Water oxidation

## 1. Introduction

One of the most important photochemical reactions in nature is the photosynthetic oxidation of water to dioxygen. This reaction is initiated by the incidence of light on the special chlorophyll, $P_{680}$, in the transmembrane protein complex called photosystem II (PS II). Subsequent oxidative steps of the oxomanganese cluster, known as the $O_2$-evolving center (OEC), result in the evolution of $O_2$ from water. With the structure of PS II still not determined, there have been intensive biophysical studies done on this enzyme. The information obtained by biophysical studies is used as a starting point for inorganic chemists, who are trying to model the active site of PS II. Inorganic modeling of the OEC in PS II is an area of active research. Researchers are synthesizing oxomanganese clusters with varying nuclearity, ligation and oxo-bridges. These systematic studies on oxomanganese clusters have been helpful in understanding some aspects of the native enzyme. Thus, there has been a productive interplay between the biophysical and inorganic studies.

With little structural information on the OEC, mimicking its chemical properties and structure is a challenge. In this review, we present the efforts in understanding the structure and function of the OEC by synthesis and study of oxomanganese model complexes. In particular, we focus our report on the various types of oxomanganese clusters synthesized to date and their physical properties.

This review is divided into six main sections. Section 2 deals with the background information on PS II, with emphasis on the OEC and its functioning. Inorganic chemists must base their efforts to model this metalloenzyme on the available information on the ligation, oxidation states and types of bridges between the metal centers. Also, mechanistic aspects of the enzyme are of great importance.